

RESEARCHES ON MODEL COMPOUNDS RELEVANT TO LINEAR
BORON-NITROGEN POLYMERS.

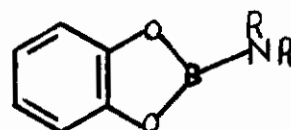
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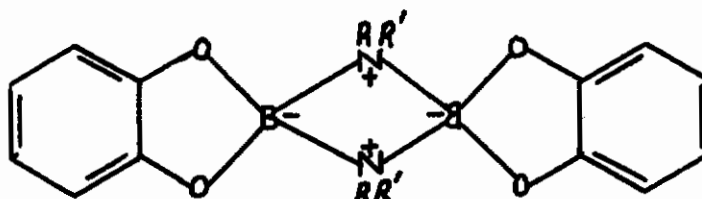
ABSTRACT

1. The following new organic boron-nitrogen compounds were synthesised:

\underline{o} -phenylene t-butylaminoboronate
 \underline{o} -phenylene ethylaminoboronate
 \underline{o} -phenylene isopropylaminoboronate
 \underline{o} -phenylene phenylaminoboronate
 \underline{o} -phenylene dimethylaminoboronate



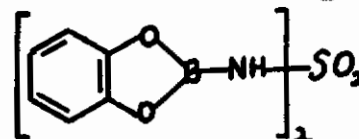
The last four compounds were all obtained as hydrolytically stable dimers.



The problem of monomer \rightleftharpoons dimer, equilibrium and the influence thereon of substituents on the nitrogen atom has been studied qualitatively.

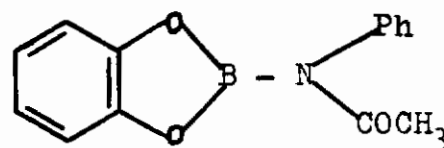
2. A preliminary study of the novel classes - acylamino- and sulphonylamino- boron compounds has been undertaken. Among the compounds characterised are

Bis(\underline{o} -phenylenedioxyboron) sulphamide

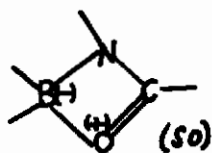


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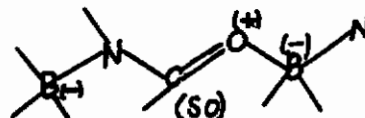
and the amides $\text{Ph}_2\text{B}\cdot\text{N} \begin{array}{l} \text{Ph}(\text{CH}_3) \\ \text{COCH}_3 \end{array}$ and



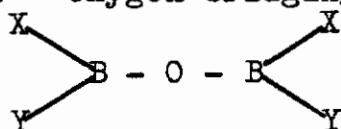
Stabilisation by chelation or autocomplexing is expected



OR



3. Oxygen-bridging is being investigated and model compounds



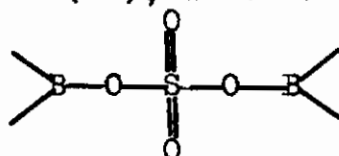
are being examined.

4. Attempts to prepare organic boron sulphates were unsuccessful.

DISCUSSION

1. BORON SULPHATES

The initial programme was concentrated on the organo-boron sulphates (II), which were (and are) unknown.



(II)

It was hoped that such compounds might be stabilized, particularly towards hydrolytic attack, by either intra-(chelation) or inter-molecular donation ($\text{O}=\text{S}=\text{O} \cdots \text{B} <$). Such chelation has previously been demonstrated to occur in the acyloxy boron compounds.¹

The synthetic routes so far investigated, all of which yielded negative results as far as boron sulphate formation was concerned, were (i) - (v).

- (i) The interaction of a boron halogen compound (*o*-phenylene chloro- or bromo-boronates, dibutyl chloroboronates or phenyldichloroborane) with dry silver sulphate in the absence or presence of various solvents (benzene, ether, acetonitrile, methylene dichloride or chloroform) under reflux.
- (ii) Potassium sulphate with *o*-phenylene chloroboronate in the

presence of liquid sulphur dioxide, under reflux.

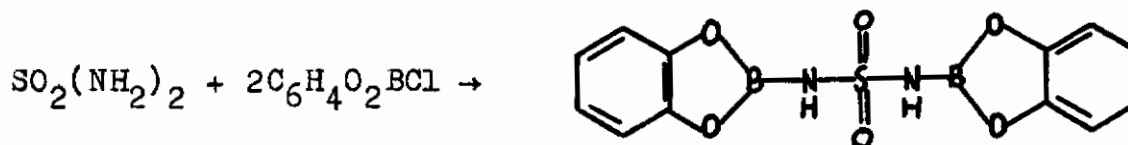
- (iii) o-Phenylene chloroboronate and dimethyl sulphate at 60° for 1 hour.
- (iv) o-Phenylene ethyl borate and sulphuryl chloride under reflux.
- (v) o-Phenylene isocyanatoboronate and mercuric sulphate in the presence of benzene under reflux.

A possible explanation for the lack of formation of organo-boron sulphates may be due to the considerable electron attracting capacity of the sulphonyl group.² Thus a sulphonyl group and a boron atom would in a boron sulphate be in competition for the electrons of the oxygen atom. In a recently published patent there is claimed the synthesis of organoboron sulphates, by refluxing dialkyl sulphates with dialkylboron chlorides, using an initial reflux temperature 100° - 150°;³ it was stated that these compounds are highly reactive and decompose above the upper reflux limit. It is proposed to repeat these experiments at a later date.

2. SULPHAMIDES OF BORON

Due to the possibility that the electron-acceptor strength of the sulphonyl group prevents sulphate formation, it was thought that if a stronger electron-donor group was attached to the sulphur, it would be possible to effect bridging of two boron atoms by a substituent containing a sulphonyl group. As sulphamic acid had previously been tried,⁴ but without success, it was decided to attempt to synthesise boron-substituted-sulphamides. In sulphamide, the diamide of sulphuric acid, it was considered that the nitrogen atoms would satisfy the requirements, and this lead to two approaches to the synthesis of boron sulphamides.

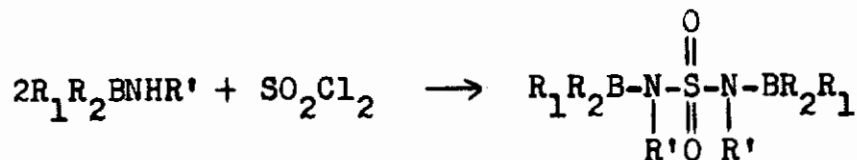
- (i) By direct metathesis of chloroboronates with sulphamide or substituted-sulphamides: thus on refluxing o-phenylene chloroboronate with sulphamide in benzene, hydrogen chloride was evolved, leaving a white benzene-insoluble solid, which analysed as the N,N'bis(o-phenylenedioxyboron) sulphamide (III)



(III)

Compound (III) was not very stable to hydrolysis.

- (ii) The second approach was to react alkylaminoboronates with sulphuryl chloride.

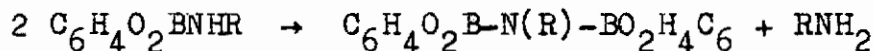


This second approach has not up to the present time been investigated, since synthesis of the o-phenylene alkylamino-boronates, which are the required precursors has lead to other interesting chemistry (see Section 3).

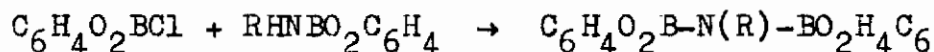
3. o-PHENYLENE ALKYL- OR ARYL- AMINOBORONATES

Investigation of o-phenylene alkylaminoboronates was undertaken partly in order to provide starting materials for borosulphamides and partly as a means of producing new boron compounds with boron-nitrogen-boron linkages. The latter problem was envisaged as involving the following alternative reaction sequences.

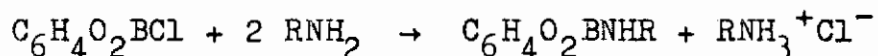
- (i) By analogy with the pyrolysis of tris(alkylamino)boranes, which eliminate amine to produce boron-nitrogen-boron linkages;² thus, it was intended to pyrolyse the o-phenylene alkylaminoboronates to give the required compounds.



- (ii) By direct metathesis between o-phenylene alkylaminoboronates and o-phenylene chloroboronates.



A number of o-phenylene alkylaminoboronates were synthesised, and two methods of preparation were used. The first method was by the reaction of o-phenylene chloroboronate and the appropriate amines in the presence of benzene or light petroleum, and subsequent removal by filtration of the amine hydrochloride.

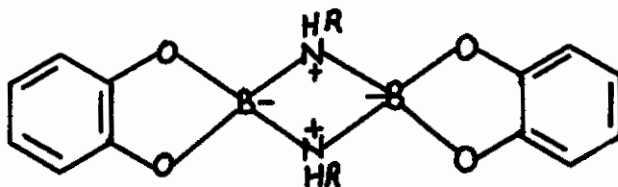


The second method of synthesis was by transaminating o-phenylene diethylaminoboronate, by the use of the appropriate amine in the presence of light petroleum. This method was preferred due to the speed and efficiency of reaction. The o-phenylene phenyl-, isopropyl-, ethyl-, and t-butyl-aminoboronates were prepared by the methods outlined. Some of the properties of the above aminoboronates are summarised in Table 1.

TABLE 1.

Compound	Ref. No.	B.p. (°/mm.)	M.p. (°)	Normal state of Aggregation	Miscellaneous
$C_6H_4O_2BNHBu^t$	IV	68/0.3		Monomer	Readily attacked by moist air
$C_6H_4O_2BNHPr^i$	V	54/0.2		Monomer = Dimer	Slowly attacked by moist air
$C_6H_4O_2BNHEt$	VI		265-75	Dimer	Stable but slowly attacked by cold water
$C_6H_4O_2BNHPh$	VII		266-8	Dimer	Stable and very slowly attacked by cold water

Structurally, compounds (V) - (VII) are considered to be dimers (VIII), due to their low reactivity, molecular weights, infrared spectra (see below) and steric requirements.



(VIII)

Compound (IV) is considered to be monomeric from similar evidence.

Infrared spectra of compounds (V) - (VII) show broad bands attributed to BN stretching frequencies at $920 \pm 10 \text{ cm}^{-1}$ which is in accord with previous observations for the BN stretching frequencies of the other similar dimer $(Me_2NBCl_2)_2$.⁶ The monomeric o-phenylene t-butyl-aminoboronate has a BN stretching frequency at $1535 \pm 2 \text{ cm}^{-1}$, which is in good agreement with BN stretching frequencies in other borazens,⁷ (including monomeric Me_2NBCl_2).⁶

The spectra of all of the dimeric compounds show rather low NH stretching frequencies at $3225 - 3125\text{cm}^{-1}$, this may be compared with the NH stretching frequency of the monomeric *o*-phenylene *t*-butylaminoboronate located at $3472 \pm 2\text{cm}^{-1}$

Compound (V), when freshly prepared and prior to distillation, was a liquid and had the BN stretching frequency at $1543 \pm 2\text{cm}^{-1}$ and the NH frequency at $3425 \pm 2\text{cm}^{-1}$. After distillation it solidified and although both these peaks still persisted to a small degree in a spectrum of the solid, the dimer peaks were very much more predominant. There thus appears to be an equilibrium between the monomeric and dimeric states for compound (V). The significant spectroscopic data are summarised in Table 2.

TABLE 2.

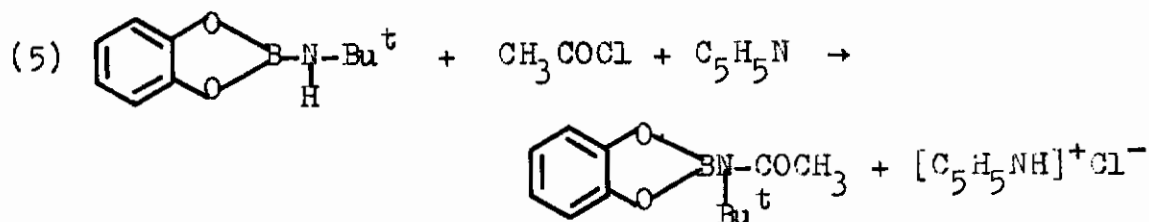
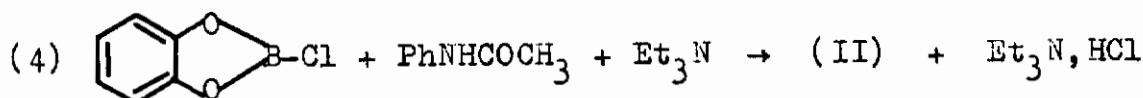
R in $\text{C}_6\text{H}_4\text{O}_2\text{BNHR}$	Bu ^{t*}	Et	Pr ^{i*}	Pr ⁱ	Ph
NH (cm^{-1})	3472 ± 2	3174 ± 2	3425 ± 2	3195 ± 2	3125 ± 2
BN (cm^{-1})	1535 ± 2	915 ± 10	1543 ± 2	922 ± 10	918 ± 10

* monomers

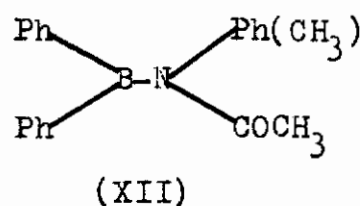
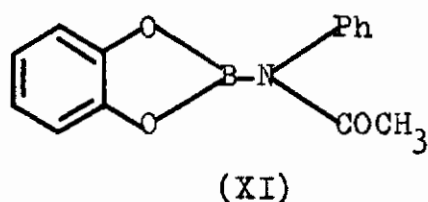
The reason for dimerisation is clearly due to the thermodynamic preference for existence in this state, but may be prevented if the steric effects of the substituent groups introduce a high entropy term. The low steric requirement of the *o*-phenylene dioxyboron ring enables the thermodynamic factor for dimerisation to be greatly enhanced. This is instanced by the fact that even *o*-phenylene isopropylaminoboronate is dimeric, despite the presence of the bulky isopropyl group.

4. *o*-PHENYLENE DIALKYLAMINOBORONATES

In the light of the discovery of the dimeric *o*-phenylene-dioxyborons described in Section 3, it was decided to investigate the dialkylamino series also. The *o*-phenylene diethyl- and di-*n*-butyl-aminoboronates had previously been prepared and were monomeric high boiling liquids,⁸ which were very susceptible to hydrolytic attack. Therefore any possibility of isolating a dimer in this series, was only likely with the lowest homologue, namely *o*-phenylene dimethylaminoboronate. This compound was synthesised by direct transamination of *o*-phenylene diethylaminoboronate with dimethylamine, using light petroleum as solvent. Distillation afforded a crystalline solid, which from molecular weight, its hydrolytic stability and molecular model consideration was assigned



Routes (3) and (4) appear promising, but the others less so. Using method (3), the amides (XI) and (XII) have been made. Their properties are being investigated.



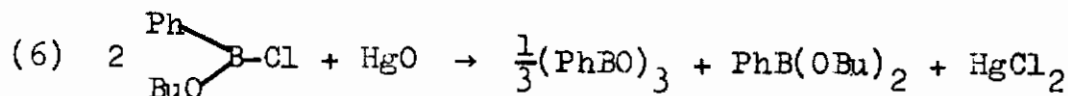
6. OXYGEN-BRIDGING

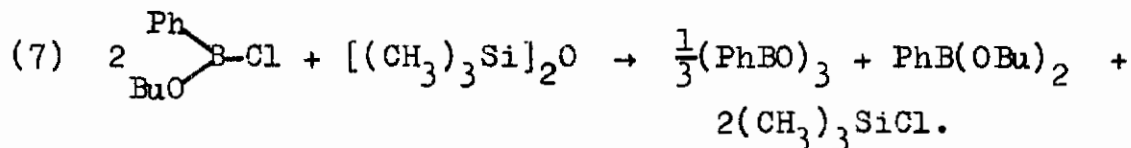
A major purpose of our research is the synthesis of model compounds for polymers, having two boron atoms attached through a bridging group. In the present case, bridging through an oxygen atom was explored.

Compounds of the type $\text{R} \begin{smallmatrix} \diagup \\ \text{X} \end{smallmatrix} \text{B-O-B} \begin{smallmatrix} \diagdown \\ \text{X} \end{smallmatrix} \text{R}$ although known are very limited in number. Examples are where $\text{R} = \text{AcO}, \text{Bu}, \text{Ph}$ and $\text{X} = \text{AcO}, \text{Bu}, \text{Ph}$ or halogen. A survey of the literature of these compounds was carried out in order to find methods to extend the series. It is proposed also to use these compounds to attempt the preparation of novel ring systems, e.g. tetrameric boroxoles.

The synthesis of $[\text{Ph}(\text{BuO})\text{B}]_2\text{O}$, (XIII), from n-butoxychlorophenylborane was attempted.

Two reaction schemes were carried out (see below), but in neither case was (XIII) isolated. It may have been an unstable intermediate, however, in reactions (6) and (7)





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